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The Interaction of Paramagnetic Relaxation Reagents with Intra- and Intermolecular Hydrogen Bonded Phenols

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16. ABSTRACT
Intermolecular electron-nuclear 13-C relaxation times (T_1^e's) from solutions containing the paramagnetic relaxation reagent (PARR), $Cr(acac)_3$, used in conjunction with 13-C T_1's in diamagnetic solutions (intramolecular 13-C - ^1H dipolar T_1's) provide a significant increase of information in studies of hydrogen-bonded liquids. Analysis of the association process with these data shows great promise in testing association models. It is also possible to determine the geometry of $Cr(acac)_3$-substrate complexation using the inverse sixth power distance dependence of T_1^e's. Several models for free and hindered internal rotation are tested for hydroxyl containing organic substrates (phenols, borneol) which are rigid at the point of attachment to the paramagnetic relaxation reagent (PARR). For symmetrically substituted phenols the observed electron-nuclear relaxation rates cannot be accounted for by a "static" model with a point locus for the PARR. Better agreement requires models with free internal rotation about the C(1)-O bond for phenol. For ortho-substituted phenols hindered rotation models appear to be superior to the "static" model. The Cr-O distances calculated evidence hydrogen bonding between $Cr(acac)_3$ and phenols. The average distance is ca. 4.9 A for 4-chloro- and 3,5-dichloro-phenol while for the rest of the phenols tested the distance is ca. 4.1 A. Calculations indicate that there may be two different types of PARR-phenol complexes. For 4-chlorophenol and 3,5-dichlorophenol solutions the average composition of the solvation sphere of $Cr(acac)_3$ appears to be quite different from the solvation spheres for the rest of the phenols studied.

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The Interaction of Paramagnetic Relaxation Reagents with Intra- and Intermolecular Hydrogen Bonded Phenols

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Intermolecular electron–nuclear ^{13}C relaxation times (T_1^e's) from solutions containing the paramagnetic relaxation reagent (PARR), $Cr(acac)_3$, used in conjunction with ^{13}C T_1's in diamagnetic solutions (intramolecular ^{13}C–^1H dipolar T_1's) provide a significant increase of information in studies of hydrogen-bonded liquids. Analysis of the association process with these data shows great promise in testing association models. It is also possible to determine the geometry of $Cr(acac)_3$–substrate complexation using the inverse sixth power distance dependence of T_1^e's. Several models for free and hindered internal rotation are tested for hydroxyl containing organic substrates (phenols, borneols) which are rigid except at the point of attachment to the paramagnetic relaxation reagent (PARR). For symmetrically substituted phenols the observed electron–nuclear relaxation rates cannot be accounted for by a "static" model with a point locus for the PARR. Better agreement requires models with free internal rotation about the C(1)–O bond for phenol. For ortho-substituted phenols hindered rotation models appear to be superior to the "static" model. The Cr–O distances calculated evidence hydrogen bonding between $Cr(acac)_3$ and phenols. The average Cr–O distance is ca. 4.9 Å for 4-chloro- and 3,5-dichlorophenol while for the rest of the phenols tested the distance is ca. 4.1 Å. Calculations indicate that there may be two different types of PARR–phenol complexes. For 4-chlorophenol and 3,5-dichlorophenol solutions the average composition of the solvation sphere of $Cr(acac)_3$ appears to be quite different from the solvation spheres for the rest of the phenols studied.

Carbon-13 spin–lattice relaxation studies have given significant insight into organic molecular structure and intermolecular interactions.[2] It has been shown that intermolecular hydrogen bonding results in motional restrictions, and consequently a shortening of ^{13}C dipolar spin–lattice relaxation times (T_1's). This result is expected since intermolecular H bonding leads to the formation of larger molecular species with slower molecular tumbling. In that way, normal ^{13}C–H dipolar T_1's can be utilized as a probe to study molecular association in solutions.

We wish to show that the combination of *intermolecular* ^{13}C T_1's in solution containing paramagnetic reagents (i.e., T_1^e's) combined with more typical T_1 measurements in diamagnetic solutions (*intramolecular* ^{13}C–H dipolar T_1^e's) give a significant increase of information in studies of solution dynamics for liquids where hydrogen bonding occurs. This is the first report to our knowledge of the use of *both* techniques to probe chemical dynamics.[3]

Paramagnetic relaxation reagents (PARR) such as tris(acetylacetonato)chromium [$Cr(acac)_3$] are good proton acceptors, hydrogen bonding to molecules with both strongly and weakly acidic hydrogens.[4-6] This interaction results in the formation of PARR–substrate complexes. Thus, along with other applications, these relaxation agents have been used as NMR spin labels to assign lines in ^{13}C NMR spectra.[7] Moreover, it is possible in principle to calculate the time-averaged PARR–substrate complex geometry from the inverse sixth power distance dependence of the electron–nuclear dipole–dipole relaxation rates.[7] An earlier determination was based on the assumption of a single point locus for the PARR center.[7] With more elaborate calculations, we will show that for some cases the single-point locus model is a very crude approximation. Indeed, for the molecules discussed in this paper the best description of the PARR–substrate complex is a model with hindered or free internal rotation, leading to the locus for the Cr nucleus to be spread out in space. These calculations show that similar problems as found for lanthanide shift reagents[8-11] exist for PARR complexes, although the latter type of complexation to organic molecules is different in its nature.

Experimental Section

Spin–Lattice Relaxation Times. ^{13}C spin–lattice relaxation times were measured with single-phase detection at 67.9 MHz (Bruker HX-270), using the unmodified inversion–recovery pulse sequence. Spectral widths of 4000–5000 Hz were used for all the cases except for solutions **9**–**11** (Table II) for which 1500-Hz spectral width were used; 8K transforms were used. Reported T_1's are averages for two runs. Internal accuracy was 2–5% for all solutions except **9**–**11** and **21**–**31** (5–10%). Particular experimental care was taken for solutions **12**–**19** and **26** and **27**. T_1^e values are determined from relaxation rates with subtraction of the diamagnetic relaxation rates.

Computational Approach for PARR Calculations. A modified version of an iterative computer program LISRIT for the simulation of LIS shifts and/or spin relaxation in NMR was used.[9] This program is very flexible and the user may try several models of his own design. The models tested in this paper are depicted in Table I.

Interatomic distances in the phenol molecule were taken from ref 12. The Cartesian coordinate system used by Armitage et al. was adapted.[8] For the phenol molecules r, Ω, and ϕ have the description shown in Figure 1.

^{13}C Chemical Shifts. The assignment of ^{13}C resonances for the phenols was achieved by comparison with shifts of phenol and by taking into account shielding parameters for substituted benzenes.[13] Those assignments are recorded in the supplementary material (see paragraph at

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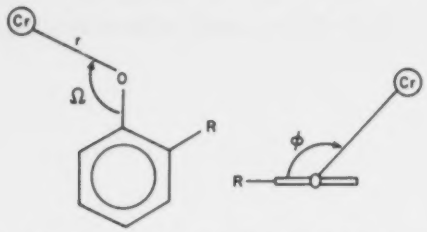

Figure 1. Definition of r, Ω, and ϕ for Cr(acac)$_3$–phenol complexation.

TABLE I

model[a]	Distribution of ϕ and populations of rotamers (in parentheses)
ST-1	ϕ (1.0)
NF-2	ϕ,[b] $\phi + 180°$ [b]
NF-3	ϕ,[b] $\phi + 120°$,[b] $\phi + 240°$ [b]
NF-4	ϕ,[c] $\phi + 180°$ [c]
MS-5	ϕ (1.0), $\phi + 90°$ (1.0), $\phi + 180°$ (1.0), $\phi + 270°$ (1.0)
MS-6	ϕ (1.0), $\phi + 120°$ (1.0), $\phi + 180°$ (1.0), $\phi + 300°$ (1.0)
MS-7	ϕ (1.0), $\phi + 120°$ (1.0)
MS-8	ϕ (1.0), $\phi + 60°$ (1.0)
RR-9	$\phi \pm 15°$ (1.0)[d]
RR-10	$\phi \pm 30°$ (1.0)[d]
RR-11	$\phi \pm 45°$ (1.0)[d]
RR-12	$\phi \pm 60°$ (1.0)[d]
RR-13	$\phi \pm 75°$ (1.0)[d]
RR-14	$\phi \pm 82.5°$ (1.0)[d]
RR-15	$\phi \pm 90°$ (1.0)[d]
RR-16	$\phi \pm 105°$ (1.0)[d]
FR-17	$\phi \pm 180°$ (1.0)

[a] For convenience, we denote the various models as follows: ST, the static PARR-substrate model; NF, n-fold axis model with populations of the sites to be adjusted (NF-2 and -3); MS, multisite model; RR, for restriction rotation; and FR, free rotation models. [b] Populations of the sites to be adjusted. [c] Each site 10° Gaussian wide at half-height. [d] Population outside this range = 0.0.

end of text regarding supplementary material). The diamagnetic and paramagnetic T_1's were used to confirm ambiguous assignments.

Results and Discussion

Effect of Hydrogen Bonding on ^{13}C T_1's (Diamagnetic Solutions). The T_1 data for the C–H carbons are shown in Table II. ^{13}C T_1's for the diamagnetic solution of 3,5-dichlorophenol (solution 1 in Table II) monitor the presence of intermolecular hydrogen bonding in this phenol. T_1's for **1** are half as long as those of the other two dichlorophenols (solutions **5** and **6**). Formation of hydrogen-bonded molecular aggregates causes the averaged molecular correlation time τ_R to be approximately twice as long and thus the T_1's are shortened. The molecular motion as probed by ^{13}C T_1 data is *not* indicated by the solution macroscopic viscosities (Table II).

The lower degree of association for 2,5- and 2,6-dichlorophenol may be explained by a combination of *intramolecular* hydrogen bonding between the phenolic OH and ortho chlorine atoms, and by steric inhibition of intermolecular hydrogen bonding. The same trends in relaxation behavior are featured for para and ortho chlorophenols (solutions **2** and **8**). Moreover, it can be seen from the relaxation data for *o*-cresol (solution **4**) that *intramolecular* hydrogen bonding is significantly responsible for "long" T_1's in ortho halophenols. For *o*-cresol, similar steric inhibition operates (cf., T_1's of phenol, solution **3**) hindering self-association, but the T_1's of 2-bromo- and 2-chlorophenol (**7** and **8**) are still twice as long as the T_1's of *o*-cresol. The ^{13}C T_1's for 2,5-dichlorophenol are somewhat shorter than those of 2,6-disubstituted phenol. If one assumes that the (averaged) correlation time for 2,6-dichlorophenol represents largely monomer and τ_c for 3,5-dichlorophenol represents a partially aggregated species, then the mole fraction of dimer may be estimated for the 2,5-dichlorophenol solution at $\lesssim$13%. This is in agreement with IR[14] and ^1H NMR[15] studies on ortho-substituted halogenated phenols which showed the existence of "cis–trans dimers" in equilibrium with the monomeric molecules. For *o*-chlorophenol the molar fraction of the dimer was estimated from cryoscopic measurement to be 10% (in benzene, 0.5 *m*).[16]

For more dilute solutions (solutions **9**, **10**, and **11**, 0.5 *m* in benzene) the relative extent of association of different phenols parallels the trends found in the more concentrated solutions. It is interesting to compare ^{13}C T_1 derived estimates of the aggregation in these three solutions with the cryoscopic determination of association at the same concentration.[16] In the cryoscopic study, contrary to the previous estimations, the phenol was found to be substantially more associated than the substituted phenols (data for model A, Table III). Considerably decreased association of phenol was obtained when the cryoscopic data were corrected for the effects of solid solution formation between phenol and benzene (model B in Table III). These two association models were therefore used in interpreting our ^{13}C T_1 relaxation data. We wished to learn to what extent the relaxation times can distinguish between these two sets of association data, thus providing an independent test for an aggregation model.[17]

From the percentage of each species present at the 0.5 *m* phenol concentration (the percentages were calculated from overall equilibrium constants in ref 16) and with the approximation that a single rotational correlation time τ_R

TABLE II: Carbon-13 Spin-Lattice Relaxation Data for Phenols in Diamagnetic Solutions

			^{13}C T_1's of C no., s				
soln[a]	compd	visc, cP	2	3	4	5	6
1	3,5-dichlorophenol	0.97	3.15		2.94		3.15
2	4-chlorophenol	1.11	3.31	3.41		3.41	3.31
3	phenol	1.01	4.06	3.87	2.62	3.87	4.06
4	*o*-cresol	*b*		4.09	3.59	4.35	3.98
5	2,5-dichlorophenol	0.88		5.75	5.17		5.94
6	2,6-dichlorophenol	0.93		6.08	6.70	6.08	
7	2-bromophenol	0.98		8.02	7.78	7.01	7.98
8	2-chlorophenol	0.87		8.82	7.55	7.71	8.51
9	3,5-dichlorophenol	0.64	6.87		7.00		6.87
10	phenol	*b*	10.06	9.95	8.50	9.95	10.06
11	2,6-dimethylphenol	0.60		10.39	10.34	10.39	

[a] The molarity of solutions 1–8 is 1.7 M in CCl_4; the molality of solutions 9–11 is 0.5 *m* in benzene-d_6. Temperature 38 ± 2 °C. Solutions 9–11 were N_2 degassed. [b] Not measured.

TABLE III: Analysis of Relaxation Data for Phenols with Different Association Models

soln	compd	^{13}C T_1(est)[c] model A (8, 76, 16)[a]	^{13}C T_1(est)[c] model B[b] (32, 46, 22)[a]	^{13}C T_1 obsd
11	2,6-dimethylphenol (87, 13, 0)[a]	11.2–13.3	10.6–11.2	10.4
9	3,5-dichlorophenol (72, 28, 0)[a]	7.4–8.8	7.0–7.4	6.9
10	phenol	7.3–8.7	8.3–8.6	8.5–10.0

[a] Percentages of monomer units in monomer, dimer, trimer species, respectively. [b] Model B was corrected for solid solution formation. The overall equilibrium constants for dimerization and trimerization (not given in ref 16) were calculated from the cryoscopic date given in Table IV and Figure 6 of ref 16. The fitting procedure to the cryoscopic data for the model B (ref 16, Table IV and Figure 6) has resulted in the following overall equilibrium constants for the association of phenol: $K_{12} = 4.42$ and $K_{13} = 9.22$. [c] Lower limit of T_1(est) obtained when the T_1(para) of phenol was used in the fit. The upper limit for T_1(est) resulted when phenol T_1(meta, ortho) were taken.

TABLE IV: Carbon-13 Spin–Lattice Relaxation Data for Phenols in Paramagnetic Solutions

soln[a]	compd	visc, cP	^{13}C T_1^{para} C no.,[b] s 1	2	3	4	5	6	$T_1^e(CCl_4)$ CCl_4	$T_1^e(CCl_4)$ / T_1^e(C-1)
12	4-chlorophenol	1.21	0.061	0.078	0.170	0.248	0.170	0.078	0.86	14.1
13	3,5-dichlorophenol	1.05	0.064	0.082	0.186	0.262	0.186	0.082	1.02	15.9
14	phenol	1.05	0.066	0.093	0.214	0.310	0.214	0.093	0.87	13.2
15	*o*-cresol	1.29	0.095	0.218	0.316	0.303	0.197	0.076	0.81	8.5
16	2,5-dichlorophenol	0.92	0.096	0.266	0.361	0.400	0.290	0.086	0.93	9.7
17	2-bromophenol	1.13	0.113	0.275	0.385	0.382	0.265	0.103	0.77	6.8
18	2-chlorophenol	0.97	0.119	0.294	0.414	0.396	0.284	0.112	0.80	6.7
19	2,6-dichlorophenol	0.95	0.192	0.306	0.370	0.346	0.370	0.306	0.79	4.1

[a] 1.7 M solutions in CCl_4 with 4.0×10^{-2} M $Cr(acac)_3$ added. Temperature 38 ± 2 °C. [b] T_1^{para} is the observed T_1 in the $Cr(acac)_3$ containing solution; quantitative interpretation requires separation of small diamagnetic components, as determined from the measurements given in Table II.

exists for each hydrogen bonded species and that τ_R is proportional to the molecular weight of the aggregate, a square fit to the observed T_1's can be calculated.[18]

The averaged T_1's were taken for the calculations, except for phenol itself, for which the relaxation times of both ortho and para carbons were used, in order to take into account the more highly anisotropic tumbling of this molecule. Thus, only the range of calculated T_1's could be obtained. Comparison of the observed T_1's with estimated values is shown in Table III. For the first set of association data, the agreement between estimated and experimental T_1's is not as satisfactory as the agreement for the second model. Clearly, the ^{13}C T_1 determination, however crude, indicates that at the concentration studied phenol is associated a maximum extent of ca. 60% of the initial concentration. Probably the percentage of association is lower than 60%, a suggestion which is in accord with the spectroscopic determinations.[19,20] At 0.4 M concentration in CCl_4, 50% of the phenol is found in monomeric form, the rest occupying two aggregated species.[20]

^{13}C T_1 Relaxation in Solutions with the Paramagnetic Additive. In solutions containing $Cr(acac)_3$ the ^{13}C T_1's are much shorter than in the diamagnetic solutions; electron–nuclear dipole–dipole interactions dominate the ^{13}C nuclear spin–lattice relaxation.[6,21] When there is intermolecular association between the paramagnetic chelate and phenol molecules due to hydrogen bonding from the OH proton to the ligands of the metal chelate this can be observed in two ways: (1) the phenol T_1^e's are significantly shorter than T_1^e for the "inert" standard CCl_4; (2) T_1^e for the C-1 and ortho carbons of the phenol close to the site of complexation are shorter than the meta and para carbon T_1^e's (see Table IV). Viewing these effects only as association between the phenols and the $Cr(acac)_3$ is somewhat simplistic (see below) since there is obviously a competition between phenol–phenol and phenol–chelate association. However, it appears that this approach suffices for the qualitative description of PARR–phenol interactions. In all of the phenols listed in Table IV, intermolecular hydrogen bonding with the $Cr(acac)_3$ molecules is evidenced. In 3,5-dichlorophenol (solution **13**) and 4-chlorophenol (solution **12**) and C-1 carbon T_1^e are ca. 15 times shorter than the CCl_4 ^{13}C T_1^e, and in phenol (solution **14**) the same ratio is approximately 13. This small difference may result from an increase in acidity for the phenolic proton in the chloro compounds. By contrast, the T_1^e for C-1 in 2,6-dichlorophenol (solution **19**) is only four times shorter than the CCl_4 T_1^e. In this case intramolecular hydrogen-bonding between the phenolic OH and the ortho chlorines competes with intermolecular association. In addition, the intermolecular association is sterically hindered by the bulky ortho chlorine atoms. The T_1's of *o*-cresol (solution **15**) are illustrative for pure steric effects which also lessen intermolecular association with the chlelate.

It is possible to study these effects by doing competition experiments, as in Table V. In solutions **20** and **21**, 3,5-dichlorophenol and 2,5-dichlorophenol were run against the unsubstituted phenol. In the 3,5-disubstituted compound the greater acidity of the phenolic OH is indicated by shorter T_1's for the C-1 and ortho carbons (by a factor of 2). In the 2,5 compound intramolecular H bonding to the 2-chlorine and steric hindrance reverse the competition between the chlorinated and unsubstituted phenols. Even addition of the third chlorine substituent at the 3 position in the phenol ring (solution **22**) does not change this situation. For solution **23**, *o*-cresol/phenol, the influence of the steric effect alone is demonstrated.

In an attempt to partially separate the steric and intramolecular hydrogen bonding effects, 2,6-dimethylphenol was used as a steric model for 2,6-dichlorophenol. Solution **24** contained both compounds. In spite of its greater acidity 2,6-dichlorophenol shows less tendency to H bond to the $Cr(acac)_3$ as evidenced by the longer T_1 for C-1 and also by the relative lack of polarization of the ring carbon T_1's (comparing the T_1's for all ring positions in both compounds of solution **24**).

TABLE V: Carbon-13 Spin-Lattice Relaxation Data for Phenols in Paramagnetic Solutions

soln[c]	compd	visc, cP	$^{13}C\ T_1^{para}$ C no.,[d] s						CCl_4
			1	2	3	4	5	6	
20[a]	3,5-dichlorophenol	1.49	0.049	0.080	0.182	0.237	0.182	0.080	0.71
	phenol		0.103	0.150	0.279	0.327	0.279	0.150	
21[a]	2,5-dichlorophenol	1.23	0.146	0.260		0.323	0.296	0.113	0.78
	phenol		0.077	0.083		0.288		0.083	
22[a]	2,3,5-trichlorophenol		0.092	0.202	0.280	0.289	(0.176)	0.066	0.58
	phenol		0.058	0.075	(0.176)	0.224	(0.176)	0.075	
23[a]	*o*-cresol	1.50	0.144	0.291	0.369		0.258	0.111	0.64
	phenol		0.101	0.120	0.257		0.257	0.120	
24[a]	2,6-dichlorophenol	1.30	0.183	0.263	0.314	0.285	0.314	0.263	0.55
	2,6-dimethylphenol		0.153	0.208	0.342	0.351	0.342	0.208	
25[a]	2,4-dichlorophenol		0.126	0.229	0.319	0.354	0.234	0.096	0.57
	2-methyl-4-chlorophenol		0.056	0.171	0.197	0.211	0.125	0.048	
26[a]	2-bromophenol	1.35	0.159	0.327	0.402	0.396	0.304	0.139	0.75
	o-cresol		0.094	0.218	0.321	0.309	0.200	0.075	
27[a]	2-chlorophenol	1.26	0.188	0.356	0.443	0.439	0.346	0.166	0.78
	o-cresol		0.091	0.221	0.329	0.319	0.202	0.077	
28[b]	2,5-dichlorophenol		0.119	0.261		0.340	0.265	0.098	0.71
	phenol		0.056	0.065		0.212		0.065	
29[b]	2,5-dichlorophenol		0.157	0.295		0.371	0.268	0.087	

[a] Molarity of the mixed phenol solutions: 1.7 M of each of the phenol in CCl_4 plus 4×10^{-2} Cr(acac)$_3$ added. [b] Molarities of the 2,5-dichlorophenol, phenol, and Cr(acac)$_3$ in CCl_4 solutions are respectively for solution 28: 0.9, 0.9, 0.04 and for solution 29: 2.55, 1.7, 0.04.

In another experiment designed to differentiate between the steric effect and intramolecular hydrogen bonding, *o*-chlorophenol and *o*-bromophenol solutions containing Cr(acac)$_3$ were examined (solution **26** and **27**). The bromine substituent is sterically larger and thus steric inhibition of intermolecular H bonding would be more effective than with an ortho chlorine atom. By contrast, bromine is less favorable as an intramolecular H-bond acceptor. Moreover, if this *intramolecular* association is the dominant cause of *reduced intermolecular* association then the *o*-bromophenol T_1's should be *shorter* than those observed for *o*-chlorophenol. This was in fact observed. T_1's for C-1 and C-6 in *o*-bromophenol were ca. 20% shorter than the analogous T_1's in *o*-chlorophenol (C-1: 0.159 s (Br, 0.188 s Cl)); C-6: 0.139 s (Br), 0.166 s (Cl); and for the internal "standard", cresol: C-1 ~0.093 s; C-6 ~0.075 s).

Thus, on evidence obtained from this PARR study of ortho halophenols, the order of the relative intramolecular hydrogen bond strengths is confirmed to be Cl > Br. The intramolecular hydrogen bonds in ortho halophenols have been investigated extensively but with conflicting results. An "anomalous" order of intramolecular hydrogen bonding strengths in the ortho halophenols (Cl > Br > F > I) obtained support from an NMR study,[15b,22] reinvestigation of the IR spectra,[23] and more recently by theoretical calculations.[24]

It is expected that for strong (inner sphere) complexation between PARR and substrate that T_1^{para} should vary as the ratio of PARR to substrate is changed. For very weak interactions the observed T_1^{para} is independent of the amount of the substrate present. Experimental dependences on the PARR and substrate concentrations are shown in Table V (solutions **28**–**31**); a substrate concentration dependence can be observed, albiet not a linear one. This is consistent with inner-sphere complexations.

Determination of the Location of the Paramagnetic Center. The determination was carried out using data in Table IV. While the calculations in this paper were successful in arriving at well-defined and chemically reasonable positions for the paramagnetic metal nucleus in a given relaxation reagent–substrate complex, the treatment rests on a number of assumptions. These are outlined below.

The observed T_1 values reflect the time-averaged and species-averaged position of the metal atom (vide supra). The exchange of molecules between free solvent and the second coordination sphere[25] is rapid enough to give observed carbon relaxation rates that are weighted averages of the relaxation rates in these two environments. Under these conditions the following expressions are appropriate:[7,26]

$$\frac{1}{T_1^{para}} - \frac{1}{T_1^{dia}} \equiv \frac{1}{T_1^{e}} = \frac{pq}{T_1^{e}(c) + M} + \frac{1}{T_1^{e}(f)} \qquad (1)$$

$1/T_1^e$ is the adjusted relaxation rate which measures the paramagnetic contribution to the observed relaxation rate in the Cr(acac)$_3$ containing solution ($1/T_1^{para}$); T_1^e(c) and T_1^e(f) are the electron–nuclear relaxation times for complexed substrate and the translationally free substrate; p is the ratio of PARR to substrate concentrations; q is the average number of coordinated substrate molecules per PARR chelate. q depends upon the equilibrium constant for formation of the complex. Since there is a large excess of substrate molecules vs. PARR, $pq >> 1$, the fraction of the solute in the bulk solvent is ≈1. A complicating factor in the equation is nonspecific relaxation for the outer coordination spheres, $1/T_1^e$(f). To a good approximation, the relaxation contribution from outer-sphere effects is the same for all carbons in these small molecules;[7,27] thus we may rewrite our equation in the computational form

$$\frac{1}{T_{1i}^{e}} = \frac{K}{r_i^6} + R_0 \qquad (2)$$

where the constant K follows from the combined Solomon–Bloembergen equations for T_1^e(c). K is a function of the magnetic moment of the paramagnetic species and the rotational correlations time τ_R (for details see the next section).[28] In principle, the calculation carried out in that manner circumvents the need for a priori knowledge of T_1^e(f) for noncoordinated phenol molecules. Thus, this parameter was not fixed during the course of the calculations. Only those simulations are permissible however, for which the calculated R_0 is in a reasonable range of R_0's for molecules the size of phenols. Usually, T_1^e(f) could be estimated from T_1^e of an inert molecule present in the solution. The inert CCl_4 is present in each measured

TABLE VI: R factors and PARR Locations for Various Models of PARR–4-Chlorophenol Complexation ($R_0 = 1.83\ s^{-1}$)

entry	%R^d	r, Å	Ω, deg	ϕ, deg	$10^{44}K^a$	model[b]
1	8.90	7.72	180.0		881.9	1
2	0.20	5.12	127.2	0[c] (0.5), 180 (0.5)	72.0	2
3	0.20	5.09	126.6	0, 180[c]	69.5	4
4	8.98	5.53	111.7[c]	90[c] (0.5), 270 (0.5)	85.7	2
5	0.20	4.57	110.6	45,[c] 135 . . .	29.4	5
6	0.27	4.69	113.4	90,[c] 180 . . .	35.7	5
7	0.20	4.91	120.9	30,[c] 150 . . .	52.0	6
8	0.24	4.64	111.7		32.7	17

[a] The units are $cm^6\ s^{-1}$. [b] Numbering system as used in Table I. [c] Calculation performed for this parameter fixed at this value. [d] Variance parameter.

solution but it is not sufficient to use T_1^e for such a molecule. This is because translational diffusion affects T_1^e. Thus, a better model would have a structure closer to the PARR substrate. The above arguments notwithstanding, the T_1^e's for CCl_4 allow us to determine the lower limit of R_0 which is $R_0 > 1.3\ s^{-1}$ ($1/T_1^e$ for CCl_4 in *o*-bromophenol solution, Table IV).

A better model for phenol molecules is fluorobenzene, for which T_1^e in CCl_4 has been measured.[6] The average electron–nuclear relaxation rate $1/T_1^e$ is $1.97\ s^{-1}$, in 2.0 M solution of fluorobenzene with 0.05 M concentration of $Cr(acac)_3$ ($p = 0.025$). Taking into account the slightly smaller concentration of PARR in our study ($p = 0.024$) R_0 is estimated to be $1.87\ s^{-1}$. It is expected that in general for all the phenols the R_0 parameter should oscillate around this value. The upper limit for the R_0 rate could be estimated from T_1^e of *o*-chlorophenol. As T_1^{para} for the most remote carbon (C-3) is 0.414 s, R_0 may not exceed the rate $R_0 < 2.3\ s^{-1}$ [$\equiv (1/0.414)\ s^{-1} - (1/8.82)\ s^{-1}$]. T_1^e(f) is generally ca. 35% longer than the observed T_1^e for remote carbons in a complexed molecule such as a phenol.[7,27] For ortho halophenols, R_0 should be thus ca. $1.7\ s^{-1}$. This is in fact very close to the outer-sphere parameter obtained from the calculations (R_0 *calculated* $\approx 1.74\ s^{-1}$) for ortho halophenols (Table VIII).

The results of the calculations for the OH-axial symmetrically substituted phenols indicated large uncertainty in R_0 determination (and r distances) (the range of acceptable solutions for R_0 was $1.0–2.0\ s^{-1}$). So this parameter had to be fixed during the calculations. R_0's of three ortho-substituted phenols were used in deriving the relationship between R_0 and the viscosity of the solutions (see Table VIII). This linear dependence was then applied to obtain the R_0's of the non-ortho-substituted phenols.

We show later that R_0 for phenols is not the same for all the carbons in the molecule. The influence of the anisotropy of R_0 on the final calculated data appears to be stronger than the influence of inequalities in τ_R^i's for the "OH-axial" phenols.

Since the substrate molecules are rigid except at the point of complexation to the PARR, a determination of the geometry of the PARR–phenol complex consists of finding the best values of theoretical T_1^e which fit to the experimental electron–nuclear rates as the spatial position of the paramagnetic center varies relative to the substrate molecule. The calculations were not performed for 2,5- and 2,6-dichlorophenols. For these phenols steric effects together with intramolecular H-bonding interactions oppose the intermolecular complexation, so that the molecules appear to have effectively two places of complexation. For example, in 2,6-dichlorophenol (solution **19**, Table IV, also solution **24**, Table V) T_1^e for C-4, e.g., the atom most distant from the OH coordination site, is shorter than T_1^e's for C-3,5.

For the rest of the phenols in Table IV steric effects reinforce the localizing effect of intermolecular complexation. In addition, for chlorophenols weak polarization effects are favorable for the preferential complexation anti to the chlorine substituent (it has been found that for mono-substituted benzenes where the substituent cannot hydrogen bond to the chelate, the metal chelate invariably orients toward the unsubstituted end of the molecule[6]).

4-Chlorophenol. The results of fits for different models are summarized in Table VI. These results are a particularly acute illustration that the axially symmetric static model is inadequate for description of the PARR–phenol (symmetrically substituted) complex (entry 1). No good fits could be obtained for this model. We consider a fit having the variance parameter $R = 4.0\%$ to be a good one (for $10^2R = 0.4$ the fit is accurate to less than 1% of the T_1's). For the best fit to the static model a physically impossible result is obtained, i.e., for the outer-sphere parameter R_0 equal to 0.0. As expected when this parameter was fixed at $R_0 = 1.83\ s^{-1}$ poor results were obtained in terms of the R variance. For this simulation the calculated relaxation rates differ more than +20% from the experimental rates. Moreover in the static model the oxygen–chromium distance appears to be physically unrealistic.

We have therefore tested other models with varied degrees of internal motions. These are the models of the multisite PARR coordination: NF, with the population of sites added as a free parameter, and MS, without the option of the adjustable populations. Immediately it is clear from the data in Table VI that this greater latitude in internal rotational position produces more reasonable fits with respect both to the agreement with experiment, R factor, and also chemical intuition. The model with jumps between ϕ values which differ by 180° (NF-2) gives sharply defined fits for ϕ equal 0, 180° (entry 2). For this model the additional parameter to be adjusted is the population of the two sites. Generally, since phenols are rather small molecules the number of adjustable parameters approaches the number of observables (six T_1^e values).[29] In order to give the results physical significance the number of adjustable parameters must be kept at the lowest possible level. It was found that the relaxation rates are quite sensitive to changes in the angles Ω and ϕ but less sensitive to changes in r distances. Naturally one can carry out the calculations with the Ω angle fixed at a single value (for example $\Omega = 110°$), which would make the fits "sharper" in terms of their sensitivity to the R factor (and remaining adjustable parameters). We have adopted, however, the policy of carrying out the calculations with as many free parameters as possible to still obtain well-defined results. Fortunately, the symmetry of the phenol molecule (for ortho-substituted phenols see below, similar considerations are valid) puts a constraint on the angular distribution of ϕ's. Moreover, for the twofold axis model the population of the sites must be "symmetry" allowed. No improvement results when a Gaussian weight factor is applied to the ϕ values (cf. entries 2 and 3). When ϕ

TABLE VII: R Factors and PARR Locations for Various Models of PARR-*o*-Cresol Complexation

model	entry	%R	r, Å	Ω, deg	ϕ, deg	$10^{44}K$[a]	R_0, s^{-1}	rotamer approx[b]
S	1	2.21	4.45	122.0	180 (1.0)[c]	19.4	2.02	1
NF-2	2	0.28	4.32	119.2	180[c] (0.94), 0 (0.06)	15.8	1.92	2
NF-3	3	0.32	4.35	117.5	180[c] (0.88), 300 (0.12), 60 (0.0)	15.4	1.89	3
	4	2.36	3.48	83.1	120[c] (0.99), 240 (0.01), 0 (0.0)	1.82	2.03	3
MS-7	5	9.82	4.39	102.0[c]	120[c] (0.5), 240 (0.5)	12.7	1.87[c]	7, 3
MS-8	6	2.29	4.27	115.2	150,[c] 210	13.7	2.03	8
RR-9	7	2.21	4.42	120.9	165[c]-195	18.7	2.02	9
RR-10	8	2.19	4.37	119.2	150[c]-210	16.7	2.02	10
RR-11	9	2.11	4.29	115.7	135[c]-225	14.3	2.01	11
RR-12	10	1.87	4.20	111.7	120-240	11.8	1.99	12
RR-13	11	1.34	4.11	107.1	105-255	9.44	1.94	13
RR-14	12	0.91	4.07	104.9	97.5-262.5	8.40	1.90	14
RR-15	13	0.41	4.02	102.0	90-270	7.44	1.85	15
RR-16	14	1.76	3.90	97.4	75-285	5.55	1.73	16
RR-17	15	32.88	3.80	102.0		5.47	2.03	17
	16	32.88	3.91	110.5	30,[c] 150 ...	7.90	2.07	6

[a] The units are cm^6 s^{-1}. [b] Numbering system as used in Table I. [c] Calculation performed for this parameter fixed at this value.

was set at 90° the minimization adjustment leads to Ω = 180° with identical values of r, K, R, and R_0 as for the static model (entry 1). A poor fit was obtained when Ω was kept at around 112° (entry 4), also the Gaussian model MS-4 for the same values of the fixed parameters Ω, R_0 as in entry 4 gave the R factor, 10^2R = 9.3. By contrast, the multisite MS models tested (entries 5–7) gave excellent fits with ϕ equal to 90°. For these fits the Cr–O distances are in accord with a hydrogen-bonding type of interaction in PARR–phenol complexes. The striking feature about the multisite models is the very wide range of the symmetry allowed ϕ values for which equally good fits could be obtained (entries 5 and 6). This feature suggests that in reality ϕ values could be spread over the entire 0–2π range. In fact, a model with this assumption of completely free internal rotation about carbon–oxygen bond leads to an excellent fit with the data (entry 8). Moreover, the results are physically well defined in terms of chemically reasonable expectation for r, Ω, K, and R_0 values. The most likely position for the Cr nucleus is at r = 4.64 Å, Ω = 112° with R_0 = 1.83 s^{-1}.

3,5-Dichlorophenol and phenol cases show similar features as the 4-chlorophenol molecule (supplementary data). In conclusion, it appears that the free rotation model is the best description for the mode of Cr(acac)$_3$–phenol (symmetrically substituted) complexation.

o-Cresol. The qualitative situation for *o*-cresol is different because of the presence of the ortho substituent (see Table VII). Simulation of the data using the static model is good (entry 1). At first sight it would appear that contrary to the previous cases, the static model is adequately describing *o*-cresol–PARR complex geometry. However, when the twofold (NF-2) and the threefold axis (NF-3) models are applied the 180° ϕ site appears to be incompletely populated (entries 2 and 3). One notes also that rotamer averaging does not give populations consistant with that expected for normal steric effects of the methyl group (entries 3 and 4). However, it may be important that a mixture of some ϕ's in addition to the 180° site leads to improvement of the agreement R factor. If one uses Hamilton's significance test tables[30] the R factor ratio between models NF-1 and NF-2 (ca. 7.8) allows one to say that the NF-2 model is statistically better at the 90% confidence level.

By contrast, no significant improvement in terms of R factor was obtained for the multisite models MS-7 and MS-8 (entries 5 and 6). We have therefore spaced the ϕ distribution over wider ranges of angles (entries 7–15).

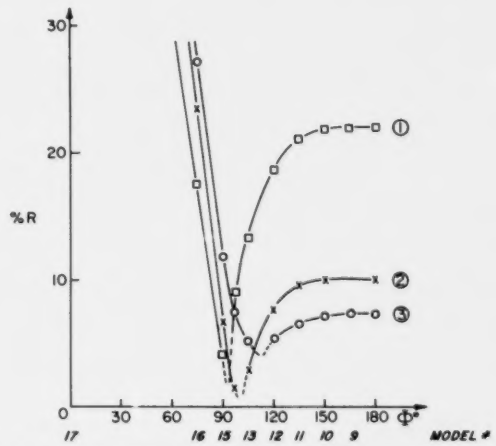

Figure 2. A graphical description of the RR models used in the simulations of relaxation data for *o*-cresol (line 1), 2-bromophenol (line 2), and 2-chlorophenol (line 3).

Starting with model RR-9 (entry 7) (actually the starting point is the static model $\phi \pm 0$), we have allowed the cone of ϕ values to increase gradually to a maximum of $0 \pm 180°$. The variance factor reaches a minimum value for model RR-15 (entry 13) and then started to rise sharply. The free rotation model (entry 15) could be rejected because of its R value. The best fit was obtained for model RR-15 although a model somewhere between RR-15 and entry 12 would give a somewhat lower R factor (Figure 2). Even so, we may conclude that the static one-site model can be rejected over the RR-15 model with a confidence level of ~98% (R = 2.20/0.41 = 4.5); moreover the NF-2 model is not better in its statistical significance (the level of significance for rejection of RR-15 over NF-2 is 50%) than the RR-15 case. It is also gratifying to find that the bond angles and r distance for the best value case (RR-15) are chemically more reasonable than the other entries.

Starting with model RR-16 (entry 14) the calculated relaxation rate for C-3 exceeds the rate for C-4. The same "reversed" trend in the calculated T_1^e pattern is observed for C-2 and C-5 carbons; $T_1^e{}_{calcd}$(C-2) < $T_1^e{}_{calcd}$(C-5), in contrast to the experimental data. For all ortho-substituted phenols in Tables IV and V the experimental T_1^{para} values and T_1^e's show the following trend: T_1(C-6) << T_1(C-5) < T_1(C-2) < T_1(C-4) < T_1(C-3). This trend of the experimental T_1's serves as an additional criterion to be

TABLE VIII: Fits of the PARR Data for the Best-Choice Models of PARR–Alcohol Complexes

entry	compd	%R	r, Å	Ω, deg	$10^{44}K^a$	R_o, s^{-1}	model[b]
1	4-chlorophenol	0.24	4.64	111.7	32.7	1.83[c]	17
2	3,5-dichlorophenol	1.53	4.56	111.7	28.6	1.72[c]	17
3	phenol	1.77	3.92	114.0	13.8	1.72[c]	17
4	*o*-cresol[d]	0.41	4.02	102.0	7.44	1.85	15
5	2-bromophenol[d]	0.30	3.70	111.2	5.11	1.78	13
6	2-chlorophenol[d]	0.55	3.76	117.5	6.09	1.70	12
7	borneol[e]	3.97	4.73	112.0	12.9	1.81	1
8	isoborneol[e]	1.52	4.62	104.8	8.38	3.14	3

[a] The units are $cm^6\ s^{-1}$. [b] Numbering system as used in Table I. [c] Calculation performed for this parameter fixed at this value. [d] The center of the ϕ angle cone is at $\phi = 180°$. [e] Relaxation data taken from ref 7. The dihedral angle ϕ is defined between two planes: one containing the oxygen atom, C-2, C-3 and the other one, C-2 and vector oxygen–PARR. For borneol $\phi = 100.5°$, for isoborneol $\phi = 229°$ (0.97), 349° (0.03). Results of calculation taken from ref 42.

TABLE IX: *R* Factors and PARR Locations for the Best Models of PARR–Phenols Complexation using Anisotropic Fixed R_o's

entry	compd	%R	r, Å	Ω, deg	$10^{44}K^a$	model[b]
1	4-chlorophenol	1.08	4.90	114.6	46.0	17
2	3,5-dichlorophenol	0.63	4.86	114.6	41.7	17
3	phenol	0.75	4.21	118.0	21.2	17
4	*o*-cresol	2.91	4.44	113.4	16.3	12
5	2-bromophenol	2.08	4.12	127.2	12.1	9
6	2-chlorophenol	1.86	4.07	129.4	11.3	1

[a] The units are $cm^6\ s^{-1}$. [b] Numbering system as used in Table I.

satisfied for a model to be acceptable. For *o*-chlorophenol and *o*-bromophenol the "reversed" trend in the calculated T_1^e's was observed starting with models RR-13 and RR-14, respectively. For each successive model (RR-14–RR-17) the calculated T_1^e's of carbons C-3 and C-2 becomes gradually shorter and T_1^e's of C-5 and C-6 longer, until for the FR-17 model the T_1(C-3) = T_1(C-5) and T_1(C-2) = T_1(C-6).

Generally, the two ortho halophenols show behavior similar to the *o*-cresol case. This is illustrated in Figure 2.

Estimation of Parameters. The results for the best-choice model for all the phenols tested are summarized in Table VIII. The constant K from eq 2 now merits some closer examination. At the magnetic field strength used, the extreme narrowing condition is approached. Under conditions where the electronic relaxation time τ_s, for $Cr(acac)_3$ is 6.5×10^{-9} s,[31] whereas τ_R, the correlation time for rotational diffusion, is approximately 10^{-11} s for complexes of the PARR–phenol size ($\tau_R^{-1} >> \tau_s^{-1}$) and with $\tau_m > \tau_R$, where τ_m is a mean lifetime in a given PARR–phenol bound state, the constant K is given by[28,32]

$$K = pq^2/_5[S(S+1)g^2\beta^2\gamma_I^2 f(\tau_R)] \qquad (3)$$

where the quantity $S(S+1)g^2\beta^2$ represents the square of the magnetic moment of the paramagnetic species, γ_I is the nuclear gyromagnetic ratio for ^{13}C nucleus, and τ_R the correlation time for rotational diffusion. One may assume that for chromium $S = 3/2$[31] and $g = 1.9802$.[33] We could now obtain the τ_R time, if only the coordination number q was accessible. Unfortunately, q is not known. This number was assigned using molecular models; the most reasonable value was assumed to be ca. 2. The PARR molecule possesses two "naked" hydrogen bond acceptor centers, each involving three oxygen atoms. Only one phenol molecule can closely and without any hindrance approach each group of oxygen atoms, resulting in the formation of the trifurcated hydrogen bond.[34] It should be pointed out that the solvation shell of $Cr(acac)_3$ is made up almost entirely of the phenol component of the phenol–CCl_4 system. This follows from the fact that the solvation shell of $Cr(acac)_3$ with the $CHCl_3$–CCl_4 system is made up almost entirely of chloroform molecules,[5] and thus it should also be true that for the phenol–CCl_4 system the shell is populated almost entirely by the strongly acidic phenol molecules.

From the K values in Table VIII the correlation times for rotational diffusion were estimated to be 30.0 and 4.7 $\times 10^{-11}$ s, respectively, for the largest and the smallest K in the table. The error inherent in our approach does not allow calculation of the exact correlation times. However, they should be of the same order as the true values. The calculated correlation times for the PARR-containing solutions are longer than for the diamagnetic solutions. Apart from the bulk viscosity effect, this is expected as τ_R for the tumbling of the phenol solvated in the complex should be longer than for the "free" solute due to the slowdown of molecular motion upon complexation with the PARR.

Different approaches to the equation describing K can yield the maximum q values. Using τ_c's of the diamagnetic phenol solutions one can calculate the maximum coordination number q. For phenols q_{max} ranges from 12 to 17.

Through our treatment of eq 2, we have assumed that deviations between the $1/T_1^e$ values for the various carbons that are found experimentally are attributed to the r^{-6} term alone; thus isotropic tumbling for the PARR–phenol complex has been tacitly assumed. The diffusional anisotropy of phenol (and, by analogy, 4-chlorophenol) tumbling is apparent in diamagnetic solutions. For the rest of the phenols, the apparent τ_R(para) is approximately equal to τ_R(ortho, meta).[35] Anisotropy, if shown in "free" solution, is presumably preserved upon complexation to the PARR (in view of our calculated results).[36] It is expected, however, that inequalities in the multiple correlation times, which arise from any internal motions and overall anisotropic tumbling of the complexes, will not be large enough to cause significant discrepancies in values of the K constants for para and ortho (or meta) carbons. Moreover, it is hoped that these diffusional anisotropies should influence the calculated results approximately to the same extent for structurally similar compounds such as the phenols. The results in Table IV support our assumptions. Contrary to the "anisotropic" 4-chlorophenol, for 3,5-dichlorophenol apparently "isotropic" molecular

tumbling is exhibited. On the other hand, both phenols show similar capabilities for self-aggregation and intermolecular complexation to the PARR. The calculated data monitors only these latter properties (cf. Tables VIII and IX).

As could be seen from Table VIII the r distances become progressively longer on proceeding from the relatively nonacidic phenols to the phenols for which strong preferential PARR complexation occurs (manifest by the shortest T_1^e's). At first notion one would expect the exact opposite results. Generally, stronger hydrogen bond interaction is coupled with a shorter hydrogen bond distance.[37]

It is important to remember, however, that the r distance obtained in the calculations corresponds to the mean hydrogen bond distance which represents an average over all hydrogen bonds present in the first solvation sphere.[38]

Since the most accessible H-bond acceptor centers in the PARR (see above) should be occupied first and the hydrogen bond formed should be the strongest one, the short r distance obtained for ortho halophenols should be well accounted for by this type of hydrogen bonding. As we previously indicated, at maximum only two phenol molecules can form this bond, both would then be relaxed to the same extent (because of the same $1/r^6$ characteristics). We denote, for purposes of brevity, this type of the complex as the "1:2" complex.[34] Proceeding further, one would expect that for p-chlorophenol the same type of hydrogen bonds occur, but in, addition, other phenol molecules may be able to hydrogen bond from more distant positions with "weaker" H bonds. We denote this type of complex as the "second shell" complex (it should be pointed out that all of these complex geometries correspond to "outer sphere" coordination, in that there is no direct bonding between the Cr nucleus and the phenols).

The results discussed above conform to the expectation that the introduction of PARR into the strongly self-associated liquids does not lead to dramatic perturbation of the solution structure. The presence of "second shell" complexes is proposed for meta- and para-substituted phenols with a sizeable percentage of monomeric species present in solutions (4-chlorophenol, 3,5-dichlorophenol; cf. Table III). For phenol itself not many monomers are available for the PARR complexation and the r distance calculated should be close to that of the "1:2" complex. Similarly, although for different reasons, with ortho halophenols the number of "trans" monomers capable of hydrogen bonding to PARR is small.

Before proceeding further, we note that the r distance trend observed above is real and not a peculiarity of the program, finding local minima. There might be an incorrect impression that shorter T_1^e's always result in longer r distances.[39] The r distance calculated depends upon the relative polarization of the T_1^e pattern in a molecule and not upon absolute values of T_1^e's. This is easily seen from the data for borneol and isoborneol (roughly for the same concentrations of PARR and alcohols as in phenol solutions),[7] Table VIII. The T_1^e's for borneol are of the order of the o-chlorophenol T_1^e's, while isoboroneol T_1^e's are twice as short.[7] As expected the r distances obtained for borneols are longer than the r's of ortho halophenols and phenol (in the borneols H bonding to the PARR's is weaker; in addition steric considerations make the "1:2" complexes predominant).

It is possible to estimate the lengths of the r distances for hydrogen bonds which exist in the solvation shell of the "second shell" complexes. Let us assume that the relaxation rates of o-chlorophenol in a complexed form $(1/T_1^e - R_0)$, which produced an r distance of 3.76 Å (Table VIII), correspond to the relaxation rates of the p-chlorophenol "1:2" complex. The relaxation rates of o-chlorophenol after taking an average of T_1^e(c) for C-2, C-6 and C-3, C-5, were subtracted from the relaxation rates for p-chlorophenol in the complexed form. The rates for this difference lead to the following results: $r = 5.32$ Å, $\Omega = 109.4°$, $K = 3.43 \times 10^{-43}$ cm^6 s^{-1}.[40] These data support previously drawn conclusions that only the formation of two or more geometries of complexes can explain our relaxation data.

The r distance obtained in the calculations is that between the phenolic oxygen and the paramagnetic nucleus. It is difficult to obtain the O (oxygen in PARR)–O (phenol) hydrogen bond lengths associated with these r distances. However, simple geometrical consideration allows us to estimate the O–O H-bond lengths involved. If one assumes that the Cr–O (phenol) r vector lies ca. 45° from the Cr–O (chelate oxygen) bonds and with this bond being 1.95 Å long,[41] simple calculation resulted in the following O–O bond lengths: 2.7 and 3.3 Å for the shortest and longest r distance in Table VIII, respectively. The lower limit on the length of an O–O H bond is around 2.40 Å and the upper limit 3.4 Å.[37a]

An O–O distance of 2.7 Å indicates rather strong hydrogen bonding which is unlikely to be involved in PARR–phenol interactions. One of the possible causes for the calculated r distances being slightly too short lays in neglecting anisotropy of the "translational" relaxation, R_0. We believe that there is no assurance that nonselective relaxation is the same for different nuclei of a molecule. Indeed, for "noninteracting" aromatics the T_1^e changes from one carbon to another. For example, for the fluorobenzene cited above the ^{13}C T_1^e's are as follows: (C-1) 0.64 s, (C-2) 0.51 s, (C-3) 0.45 s, (C-4) 0.48 s.[6] Exactly the same T_1^e pattern is observed for neat benzonitrile [Cr(acac)$_3$ concentration of 0.05 M].[7] Although it is almost impossible to know to what extent the T_1^e(f) changes for different carbons in phenols, an approximate solution seems to be possible. Since for phenols T_1^e(f) is due to random encounters of PARR and the species outside the solvation sphere it seems reasonable to expect that the relative change of T_1^e(f) from one carbon to another should be smaller (or maximally equal) than for the "noninteracting" substituted benzenes, for which much of the observed T_1^e values is due to random encounters in the first solvation sphere. We have assumed that the relative change in the R_0's in phenols is the same as in the fluorobenzene. Further, the next assumption is that the R_0's obtained from the previous calculations (Table VIII) are the averages of the "real" R_0^i's for the six carbons of phenol molecules. In this way, we could obtain the distribution of the R_0^i's among different carbons. Now, we can subtract these outer sphere relaxation rates R_0(i)'s from the $1/T_1^e$'s of the respective carbons of the molecule in two ways, depending on whether the OH group is oriented toward or away from the PARR center. Immediately it could be realized that for the latter orientation the "subtracted" relaxation rates would lead to r distances even shorter than those obtained in the first approximation (diminished polarization of the relaxation rates along the carbons in the phenol ring). The former arrangement leads to the expected improvement of the data in terms of the r distances. The final results are shown in Table IX. For the ortho-substituted phenols, the R_0^i's were estimated by adding the R_0^i's for two orientations of the phenols: one with OH pointing toward the PARR and the other with methyl or halogen orienting this substituted end of the

molecule away from the PARR center. The average then was taken between these two arrangements.

The final r distances (Table IX) now appear to be more nearly optimized. Nonetheless, the previously discussed trend in the r values is maintained.

We conclude that if one makes the assumption that the R_0^i's are the same for different nuclei of a phenol molecule, then r distances may be determined which are quite reasonable, especially when compared to one another. A further conclusion from this discussion is that preferential ordering of the solute beyond the second sphere, although small, is large enough to be observable. This interaction falls off as rapidly as r^{-4}. In estimating that part of $1/T_1^e$ which is due to interactions beyond the second sphere, a geometrical factor of $4\pi r^2$ must be taken into account.[26a] This allows for the increasing number of substrates which can be contained within a shell of fixed thickness as the radius increases.

Most interestingly, our results suggest that beyond the first solvation shell of $Cr(acac)_3$, phenol molecules are preferentially oriented with the hydroxy proton on the average closer to the PARR than the C–H ring protons.

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Supplementary Material Available: Tables containing chemical shifts for all phenol solutions; relaxation rates $(1/T_1^e)$; calculation data corresponding to Figure 2 as well as results for phenol and 3,5-dichlorophenol; tables indicating inferred precision of the PARR determination; the outer-sphere parameters $R_0(i)$'s; *o*-cresol results using the anisotropic $R_0(i)$; other additional computational results (23 pages). Ordering information is available on any current masthead page.

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